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3,546,035

**AMMONIUM NITRATE-SMOKELESS POWDER
BLASTING AGENT CONTAINING SODIUM
NITRATE-UREA AS A CRYSTALLIZATION
INHIBITOR**

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4 Claims

ABSTRACT OF THE DISCLOSURE

Crystallization-resistant blasting slurries of the ammonium nitrate-smokeless powder type having, in combination, sodium nitrate and urea as the crystallization inhibitor.

BACKGROUND OF THE INVENTION

This invention relates to slurry type blasting agent compositions. In a particular aspect, it relates to blasting agent compositions resistant to low temperature crystallization.

Aqueous blasting slurry compositions consisting primarily of inorganic nitrate, sensitizer and gelling agent, plus various additives in small amount are well known in the explosives industry. They have a high density and good cohesive properties and can be charged into wet bore holes without undue risk of dilution. Slurries using smokeless powder as the sensitizer are disclosed by F. B. Clemens in U.S. Pat. 3,235,425.

Blasting slurries of this general type have been used in large volume but they have suffered from the disadvantage that, when formulated in the lower water concentrations, the ammonium nitrate tends to crystallize in cold weather. As a result segregation and low sensitivity may occur, the slurry may not fill the hole properly and may even set up to a hard mass. Since blasting operations can otherwise be conducted at relatively low temperatures, it is desirable to employ a slurry which is formulated with a minimum of water, yet resists crystallization.

This problem with respect to ammonium nitrate slurries formulated with coarse TNT grains as the sensitizer was resolved by Cook, U.S. Pat. 2,930,685, by using either sodium nitrate or urea, but not both, in an amount of 1-25% to lower the melting point of the slurry.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a slurry-type blasting agent composition.

It is another object to provide an ammonium nitrate-smokeless powder blasting agent composition resistant to crystallization at low temperatures.

Other objects of this invention will be obvious to those skilled in the art.

It has now been discovered that, by incorporating a combination of urea and sodium nitrate into slurry-type blasting agents formulated with ammonium nitrate, smokeless powder as the sensitizer, a gelling agent and water, compositions are obtained which are resistant

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to crystallization at below-freezing temperatures. These compositions do not set up to a solid mass, nor segregate nor undergo phase separation under most of the climatic condition encountered during blasting operations.

DETAILED DESCRIPTION

The present invention provides a method of inhibiting crystallization of ammonium nitrate-smokeless powder slurry-type blasting agents to temperatures as low as about 12-14° F. The invention is contemplated as having special utility with compositions comprising primarily, from about 20 to about 35% by weight of ammonium nitrate, from about 30 to about 35% of smokeless powder, from about 15 to about 20% water, and from about 0.2 to about 3% of one or more gelling agents. Finely divided aluminum may also be employed with such compositions, as is known.

The sodium nitrate-urea combination is used in a ratio of from about 4 to about 12 parts by weight of sodium nitrate to about 1 of urea, preferably from about 4-6:1. The combination is incorporated in the slurry in a proportion of about 0.4-1.4 parts per part by weight of ammonium nitrate. Usually the proportion is in the range of about 0.7-1.2:1, and a ratio of about 1:1 is particularly preferred.

In a preferred composition, the ammonium nitrate is present at from about 20-30%, sodium nitrate at from about 12-20%, urea at from 4-5%, the smokeless powder at from about 30-35%, water at from about 15-20% and thickening agent about 0.6%.

The ammonium nitrate and sodium nitrate suitable for use in the practice of this invention can be any grade which is generally useful in blasting agent slurries. This includes the ordinary commercial grades. Preferably the ammonium nitrate is uncoated, i.e. it is free from the coating generally applied to fertilizer grade material to reduce its hygroscopicity.

The urea suitable for the practice of this invention can be any grade of commerce, and generally the lowest in cost is preferred. The grade used in fertilizer compositions is a preferred grade. Generally, the urea is present to the extent of from about 1% to about 7% by weight, preferably 4% to 6%, based on the weight of the total composition.

Smokeless powder is a preferred sensitizer for the practice of this invention. It is a well known explosive, being the basic propellant commonly used for artillery shells, small arms ammunition, and the like. It is available in several forms, commonly referred to as single base, double base, and triple base, for example. It is basically cellulose nitrate but may contain nitroglycerin and other ingredients. Smokeless powder is made and stored in large quantities for military use but tends to deteriorate somewhat on aging and, as a consequence, it may ultimately become unsafe or unreliable for use in its military applications. However, it frequently will still serve very well in blasting slurries. The use of smokeless powder in blasting slurries is discussed at length by Cook et al., U.S. Pat. 3,331,717, which discussion is incorporated herein by reference thereto. Ball powder is a special form of smokeless powder and is a particularly preferred sensitizer.

The gelling agent used may be any of those materials, or a mixture thereof, which are capable of setting up the aqueous mixture in a gel-like consistency or in the form of a relatively thick cohesive paste as is known in the

Jaguar 100 manufactured by Stein Hall Co. The slurries had satisfactory sensitivity and velocity and showed good crystallization resistance, particularly at 3-5% urea. The compositions were as follows:

Ingredients, percent by wt.:	Example No.							
	1	2	3	4	4a	5	6	7
Urea.....	1.0	2.0	2.9	3.8	4.0	4.5	4.8	5.9
Ammonium nitrate.....	32.5	30.2	28.0	25.8	21.8	19.8	23.6	19.6
Sodium nitrate.....	11.6	13.6	15.4	17.2	19.0	20.0	18.9	25.0
Ball powder.....	34.5	34.45	33.7	33.4	35.0	35.0	33.1	34.0
Water.....	19.65	10.0	19.3	19.1	20.0	20.0	18.9	14.8
Gelling agent.....	0.75	0.75	0.7	0.7	0.7	0.7	0.7	0.7
Ratio NaNO ₃ :urea.....	12:1	7:1	5:1	4.5:1	4.8:1	4.4:1	4:1	4:1
Ratio NaNO ₃ plus urea:AN.....	0.4:1	0.5:1	0.7:1	0.8:1	1.1:1	1.2:1	1:1	1.24:1
Sensitivity to C-4, g.....	10	15	15	15	15	25	10	140
Velocity, ft./sec.:								
3'					18,550		15,820	18,000
2'					18,525	16,000		10,850

¹ Tetryl.

art. The gelling agent can be one of the well-known gums such as guar, okra, or locust bean, or it can be any of the synthetics known to the art. It may be supplemented with other gelling agents or thickeners such as wood flour, cellulose ester gum and the like. Preferably, a mixture of two or more gelling agents or thickeners is used in an amount sufficient to impart the desired consistency to the slurry. The preferred consistency maintains all components, including solid materials, uniformly distributed in the slurry over an extended period of time.

The final consistency is preferably one which gives a cohesive, but pourable, mass. The effectiveness of the gelling agent varies greatly and it is within the skill of one familiar with their performance characteristics to use an appropriate amount consistent with the amount of water incorporated in the wet blasting agent.

In addition to the principal constituents listed above, other additives such as aluminum flakes or powder, micro-balloons, or zinc oxide can be incorporated as is known in the art.

Most of the compositions of the invention are insensitive to detonating action of a No. 8 commercial blasting cap, but are detonatable by conventional "booster" charges of PETN (pentaerythritol tetranitrate), RDX (cyclotrimethylenetrinitramine), Pentolite (PETN-TNT, 50/50), tetryl, Composition B (RDX-TNT 60/40), gelatin dynamites and the like.

The practice of this invention is further illustrated by the following examples. In these examples velocity was determined using schedule 40 steel pipe of the size shown.

Sensitivity to initiation was tested by detonating C-4 military explosive (consisting of RDX 91%, plasticizer 5.3%, polyisobutylene 2.1%, and motor oil 1.6%) in contact with the slurry in increasing 1 g. increments until detonation of the slurry occurred.

The texture and crystallization resistance was determined by storing samples of the slurries at 14° F. and judging their consistency.

Examples 1-7

Blasting slurries employing ball powder as the sensitizer were prepared with a combination of sodium nitrate and urea as the crystallization inhibitor. The sodium nitrate varied from about 12-25% by weight of the slurry and the urea from about 1 to 6%. The ratio of sodium nitrate to urea varied from about 4:1 to about 12:1, and the ratio of the combination to ammonium nitrate varied from about 0.4:1 to about 1.24:1. The gelling agent used was

Examples 8-11

Blasting slurries employing ball powder plus fine aluminum granules were prepared using, except for Example 11, 4% urea and 19% sodium nitrate, known from Example 4 to give crystallization resistance at 14° F. The gelling agent used was Jaguar 100 manufactured by Stein Hall Co. The ratio of sodium nitrate to urea was 4.8:1 and the ratio of the combination of sodium nitrate plus urea to ammonium nitrate was 0.9-1.1:1. In Example 11 the proportion of sodium nitrate was increased to 25%, giving a NaNO₃:urea ratio of 6:1, and a ratio of the combination to ammonium nitrate of 1.4:1. The slurries had good sensitivity and velocity and satisfactory crystallization resistance. The compositions were as follows:

Ingredients, percent by wt.:	Example No.			
	8	9	10	11
Urea.....	4.0	4.0	4.0	4.0
Ammonium nitrate.....	21.3	26.3	25.3	20.0
Sodium nitrate.....	19.0	19.0	19.0	24.8
Ball powder.....	30.0	30.0	30.0	30.0
Water.....	20.0	15.0	15.0	15.0
Gelling agent.....	0.7	0.7	0.7	0.7
Zinc oxide.....			1.0	0.5
Aluminum.....	5.0	5.0	5.0	5.0
Ratio NaNO ₃ :urea.....	4.8:1	4.8:1	4.8:1	6:1
Ratio NaNO ₃ plus urea:AN.....	1.1:1	0.9:1	0.9:1	1.4:1
Sensitivity to C-4, g.....	25	10	10	10
Velocity, ft./sec.:				
3'	20,100	17,600	16,000	18,000
2'	16,750			15,650

Example 12

The experiment of Example 4a was repeated except that TNT was substituted for ball powder as the sensitizer. The gelling agent was Jaguar 100. The resulting composition had good crystallization resistance at 14° F. and a velocity of 17,600 ft./sec. in 3" x 30" pipe.

Examples 13-14

Blasting slurries employing smokeless powder as the sensitizer and formulated with 15% water were prepared with 6% urea and 25% sodium nitrate. The gelling agent was a mixture having a ratio of about 1:2 by weight of guar gum (EXFC 50 H) and a high molecular weight polyacrylamide (Polyhall 405 M) both manufactured by Stein Hall Co. The compositions showed good crystallization resistance at low temperatures, and good sensitivity and satisfactory velocity. Example 13 is a composite of 3 replicate tests using ball powder as the sensitizer. In Ex-

ample 14, FNH smokeless powder was the sensitizer. The compositions were as follows:

Ingredients, percent by wt.:	Example no.	
	13	14
Urea	6.0	6.0
Ammonium nitrate	18.0	18.0
Sodium nitrate	25.4	25.4
Ball powder	35.0	
Water	15.0	15.0
Gelling agent	0.6	0.6
FNH		35.0
Ratio NaNO ₃ :urea	6:1	6:1
Ratio NaNO ₃ plus urea:AN	1.2:1	1.2:1
Sensitivity to C-4, g.	(4)	15
Velocity, ft./sec.:		
3	16,850	16,050
2 ¹	18,300	(2)
1 ²	14,940	

¹ 90 g. tetryl, No. 6 EBC.

² Fail.

What is claimed is:

1. A method of inhibiting crystallization of a slurry-type blasting agent at temperatures as low as 14° F., said blasting agent consisting essentially of ammonium nitrate, smokeless powder, water, and gelling agent, consisting of

incorporating in said slurry a combination of sodium nitrate and urea having a ratio of from about 4 to 12 parts by weight of sodium nitrate to about 1 of urea, said combination being incorporated in a ratio of about 0.4 to 1.4 parts per part by weight of said ammonium nitrate.

2. The method of claim 1 wherein the combination consists of a ratio of from 4 to 6 parts of sodium nitrate per part of urea, by weight.

3. The method of claim 1 wherein the combination is incorporated in the slurry in a ratio of 0.7 to 1.2 parts per part of ammonium nitrate, by weight.

4. The method of claim 3 wherein the ratio is 1:1.

References Cited

UNITED STATES PATENTS

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